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A fundamental study of clay drying using ware of large cross section

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Department:

A FUNDAMENTAL STUDY OF CLAY DRYING USING WARE OF LARGE CROSS SECTION

BY

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A

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INTRODUCTION

The drying of clay has been studied extensively in the past by many investigators, some of whom attempted to relate this information to the structure of clay and thereby develop a more vivid picture, while others studied the mechanism of drying in its own right in order to present a useable theory that would allow improvements in the drying operation.

At present the literature is unable to present a theory of the mechanism of drying that is sufficiently general to cover the observed aspects of clay drying. Many and varied mechanisms are presented, but correlation is seldom completely evident between separate investigators.

It is without question that the drying process is divided into two portions; (1) in which the rate of water loss is a constant and (2) in which the rate of water loss is not a constant but is decreasing in magnitude.

This first drying period is designated the zone of constant rate, which appears as a straight horizontal line when the rate of water loss is plotted as the ordinate and percent water content of the sample (dry basis) as the abscissa. The second drying period or the falling rate zone is a key to the drying mechanism and is open to the most question. Norton has pictured this zone as a smooth curve slightly concave upward extending from the end of the constant rate zone to the origin. This indicates that the decrease in the rate of water loss is nearly uniform on a percent water content basis. Sherwood indicates that this falling rate zone may be separated into two parts, the first

of which may or may not be a straight line while the second is slightly concave upward.

Norton also indicates that the shrinkage of the clay in drying when plotted against water content begins as soon as drying is initiated and reaches zero in the order of 20% water content. It is the purpose of this investigation to determine the nature of the falling rate zone, and the water content where shrinkage ceases in order to better define the drying mechanism for clay.

It is significant that much of the investigation into the mechanism of drying has been done on relatively small samples that may or may not characterize the drying nature of the clay itself. This study has been undertaken using samples of spherical shape whose plastic weight is in the order of 3000 grams and whose maximum wall thickness is 6 inches. It is believed that using samples of large cross section with minimum surface to volume ratio will provide more distinct definition of the particular rates at which water is lost.

Equipment has been obtained that will allow control of the wet bulb temperature, the dry bulb temperature, which in turn fixes the percent relative humidity, and the air velocity. An automatic means of recording weight loss as a function of time, and shrinkage as a time function has been built.

REVIEW OF THE LITERATURE

In 1929 T. K. Sherwood[1] concluded that the mechanism of the drying of a solid falls into three general catagories. These are:

Case I. Evaporation of the liquid at the solid surface; resistance to internal liquid diffusion small as compared with the resistance to removal of vapor from the surface.

Case II. Evaporation at the solid surface; resistance to internal diffusion of liquid great as compared with the resistance to the removal of vapor from the surface.

Case III. Evaporation in the interior of the solid; resistance to internal diffusion of liquid great as compared with the total resistance to the removal of vapor.

The text of his discussion is as follows:

The drying of a particular material need not be restricted to one of these general classifications but depending upon the initial liquid content and the drying conditions may exhibit either one, two or all three of these during any drying cycle. The drying conditions are defined as the dry bulb temperature, the relative humidity and the air velocity, all of which determine the rate at which liquid may be converted to vapor and removed from the solid.

The drying of very wet solids under constant drying conditions exhibit a period during which the rate of drying is constant. At some liquid content which is termed the critical liquid content,

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(1) Sherwood, T. K.
"Drying of Solids"
Industrial and Engineering Chem. 21, 12 (1929) 21, 976 (1929).

the rate of drying ceases to be a constant and becomes the falling rate period. In general then two distinct zones are present, the zone of constant rate and the falling rate zone. The constant rate zone is an example of Case I while the falling rate zone is an example of either Case II or Case III or both depending upon whether or not a break in the curve appears. This critical liquid content appears at 16.5% water on a 7.0 x 7.0 x 2.54 cm block, dried at room temperature in a small flue through which air was forced at 50 feet/sec., and at 8% on the same block where no forced convection was utilized. As a consequence then the same clay dried between 16.5% and 8% by two distinct mechanisms, Case I and Case II.

The Zone of Constant Rate

During the constant rate period the evaporation takes place at the surface of the wet solid, the rate of drying being limited by the rate of diffusion of water vapor through the surface film and out into the main body of the air. The drying in this period is similar to the evaporation of water from a free liquid surface and the solid assumes a constant equilibrium temperature which is the wet bulb air temperature. In this instance the latent heat of vaporization is supplied by conduction through the same surface air film through which the vapor diffuses.

Additional heat supplied either by radiation or conducted from adjoining dry surfaces, increases the equilibrium wet bulb temperature and in turn the rate of drying.

The Falling Rate Period

The typical falling rate period for numerous solids is divisible itself into two distinct zones. This shape of the rate of drying vs. percent liquid content curve is characterized by a linear portion although this need not be the case and a lower portion which is slightly concave upward. The initial portion is termed the zone of decreasing wetted surface, while the final is the zone of internal liquid diffusion controlling. It has been shown by Chang[2] that the relative humidity influences the drying rate during the constant rate zone and also during the zone of decreasing wetted surface but not during the time when internal liquid diffusion is controlling. This indicated that during or at the beginning of the zone of internal liquid diffusion controlling the plane of vaporization recedes from the surface into the material, and drying is no longer influenced by the relative humidity. The rate of drying in this zone is inversely proportional to the thickness of the material.

Norton[3] indicates that water evaporated from clay must come mainly to the surface through the fine interconnecting channels, and the rate of this flow through a piece rectangular in cross section is given by:

$$\text{Volume rate of flow} = k \frac{\text{driving force}}{\text{flow resistance}}$$

$$\text{or} \quad \frac{dV}{dT} = \frac{k(C_2^1 - C_1^1)}{l} \cdot \frac{P}{n}$$

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(2) Chang - Chemical Engineering Thesis submitted to the faculty of Massachusetts Institute of Technology (1928).

(3) Norton, F. H. "Elements of Ceramics" Cambridge, Mass., Addison - Wesley Press 1952 pp. 106-114.

where $\frac{dV}{dT}$ is the volume rate of flow C_1^1 is the water concentration on the wetter face and C_2^1 is the water concentration on the dryer face, k is a constant, l is the length of path, P is the permeability of the body and n is the viscosity of the water.

Sherwood and Comings[4] state that water moving to the surface of a solid encounters four diffusional resistances: the resistance to the movement of liquid in the interior of the solid, the resistance to diffusion of water vapor through the air filled passages, the resistance to vapor diffusion offered by the air film and the eddy-diffusional resistance of the turbulent air stream. They indicate that liquid movement takes place generally under the influence of pressure difference, due to gravity, an applied external force or capillarity, and in the drying of ordinary solids pressure difference due to gravity or similar forces are seldom encountered and any liquid movement is apparently due to cappillarity. They depict the capillarities as having smaller openings on the end exposed to the surface than at the interior. Water then evaporates from the small Menisii at the surface. The small surface Menisii then exerts sufficient capillary pull to draw water through any passages ending in air water interfaces of larger curvature. The water drawn to the surface is necessarily replaced by air which enters the solid through larger passages which are connected to larger surface openings. Water will then continue to rise to the surface through any system of interconnecting passages until all the

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(4) Sherwood, T. K. and Comings
"Moisture Movement by Capillarity"
Industrial and Engineering Chem. 26, 1096 (1934).

various Menisii at the lower ends of the water column have the same radius of curvature as the small Menisii at the surface through which evaporation is taking place.

As the drying proceeds, a time will be reached when the Menisii at the lower ends of the water column in any system of interconnecting passages are in general about the same size as the smallest cross section of the surface openings and water will no longer be drawn to the surface through these passages. Evaporation will continue from the surface Menisii, and the water in these surface openings will be depleted, thus causing the retreat of the surface Menisii into the solid. The rate of drying will consequently be retarded because of the necessity of the vapor formed to diffuse an appreciable distance through the air filled passages to the surface.

The capillary tensions developed are of considerable magnitude. If a porous alundum cup is filled with water and connected by a water column to a mercury manometer, evaporation from the small openings near the surface will develop sufficient tension to lift the mercury column a height corresponding to a tension of greater than one atmosphere.(5,6)

Westman(7) developed an apparatus to measure the capillary suction of several clays, thinking that when the mechanism of water movement to the surface was fully understood, the overall mechanism of drying

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(5) Richards, L. A. - Journ. Agr. Research 37, 719 (1928).

(6) Westman, A. E. R. "The Capillary Suction of Some Ceramic Materials." Journ. Am. Cer. Soc. 12, 585, (1929).

(7) Westman, A. E. R. - Ibid.

would be more evident. By utilizing the capillary suction produced by evaporation of water from a clay surface, water at atmospheric pressure was made to enter a steel bomb in which the gas pressure was maintained at 200 lbs. per sq. inch. He showed that capillary suction decreased rapidly with the increase in flint and feldspar in a ceramic body, and that ball clay has a quantitative value for capillary suction at least three times as great as kaolin.

Steger(8) gives a rather complete picture of the mechanism involved in first wetting and then drying a clay mass and it is of interest to summarize his views here.

Clay particles are considered to be porous, that is each individual particle contains void spaces.

(1) The first addition of water (a) to a dry clay mass goes to filling these particle pores.

(2) A second addition of water (b) will give each particle a surface film of water which may be treated as an adsorbed layer around each particle. The sum of (a + b) is known as capillary water.

(3) A third addition of water (c) goes to fill the voids between the clay particles. The voids constitute the inner particle spaces. At this stage of wetting the clay mass is rigid and non-plastic.

(4) Further addition of water causes the clay mass to swell and to become plastic. The water causes the hydrates of the clay particle to absorb water and increase in size. The water layer separates the clay particles and becomes the continuous phase.

(8) Steger, "The Theory of Drying" Tonind Ztg. 50, 28, (1927).

The suitable addition of water (d) to give a plastic mass of normal consistency may be considered the water of plasticity.

(5) The total addition of water (e) required to give a plastic mass of normal consistency may then be subdivided into the catagories given above.

$$e=a + b + c + d$$

or using the nomenclature adapted above, the total water addition for normal consistency goes to (a) fill the particle pores, (b) to coat each particle with an adsorbed layer of water, (c) to fill the inner particle spaces and (d) to float the clay particles apart with the water of plasticity.

In drying, the operations indicated in the wetting process are reversed in order, there being two main periods.

(1) The removal of the water of plasticity (d) causes the clay mass to become rigid and non-plastic. The loss in weight is proportional to the time of drying, the rate of evaporation of water from the clay being proportional to the difference between the saturated vapor pressure existing at the temperature of the clay and the vapor pressure of the air. A point is reached where no more moisture is lost at atmosphere conditions although water is present in the mass.

(2) With water of plasticity removed, the vapor pressure of the clay mass is now no longer equal to the saturated vapor pressure of water at the temperature of the clay but actually lower. In order to remove the moisture content (a + b + c), the vapor pressure of the clay mass must be raised by heat. The loss is accomplished in the order c, b, a.

The above conclusions of Steger are presently accepted with exception made for the clay particles themselves having water fillable voids.

EXPERIMENTAL APPARATUS

The problem under consideration involves the measurement of weight loss or water loss from the sample as a function of time and the corresponding shrinkage that occurs simultaneously also as a time function. With the initial plastic weight and the final dry weight being known, then the rate of water loss may be plotted vs. percent water content. To be of significance the rate of water loss must be measured under the same drying conditions from initiation of the cycle to completion. The above necessitates the use of a dry bulb temperature control and wet bulb temperature control, with corresponding recorder.

The wet bulb temperature is maintained by the addition of steam under 5#/sq. in. pressure directly into a plenum chamber located below the dryer cabinet. Correct steam additions to the system are controlled by a Minneapolis Honeywell series 90 modulating temperature controller operating a modutral motor driven steam valve. The wet bulb temperature limits are between 100°F and 210°F. The sensitive element for this instrument is enclosed by a porous tube from which water is allowed to continuously evaporate. The heat sources are, 2 sets of 6 each Chromalox Resistance units, which provide more than ample heat for drying. The dry bulb control is a Chromalox off-on liquid expansion type with a range from 150°F to 550°F.

A Brown two pen recorder is utilized to record both the wet and dry bulb temperatures. Air circulation is provided by a 110 cfm centrifugal blower, which continuously circulates the air from the

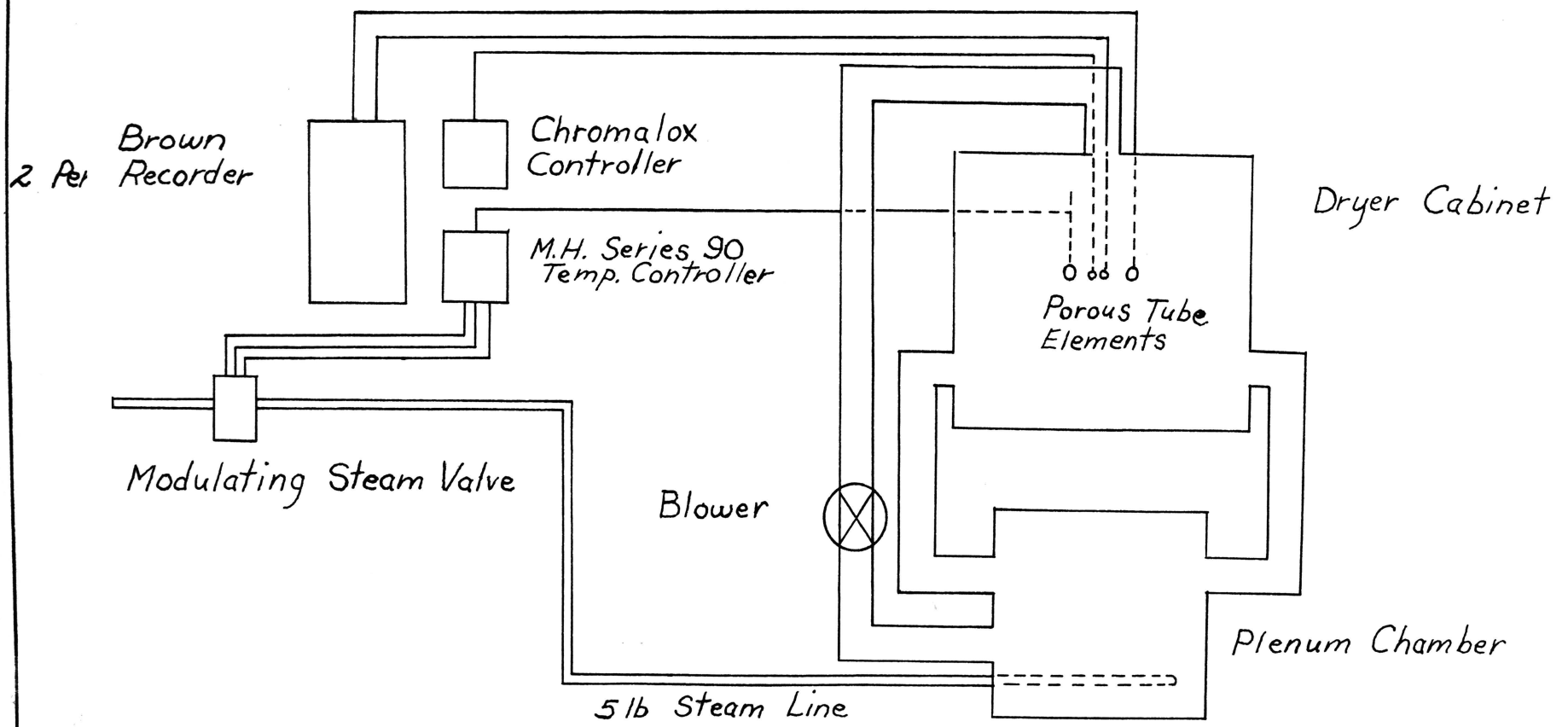
plenum chamber where it is tempered with steam to the dryer cabinet where it is heated by the Chromalox units placed directly in the air stream. A Schematic diagram is shown in Figure 1.

Weight loss as a function of time is obtained by a folded beam Chainomatic balance. As the sample loses weight, a traveling nut on a vertical threaded shaft is caused to move upward, subtracting chain length that hangs vertically from the folded beam. After the balance has detected weight loss, the traveling nut moves until the chains are once again in static equilibrium with the sample on the pan.

The motor drive for the Chainomatic mechanism is coupled to a threaded horizontal shaft and then through a bevel gear box to the vertical shaft. On the horizontal threaded shaft is another traveling nut upon which the recording pen is located. The pen extends over a drum chart that is moving at one revolution per 24 hours. Any unbalancing then caused by water loss moves the pen on the drum, producing a pattern of weight loss horizontally versus time vertically. A Schematic diagram is shown in Figure 2.

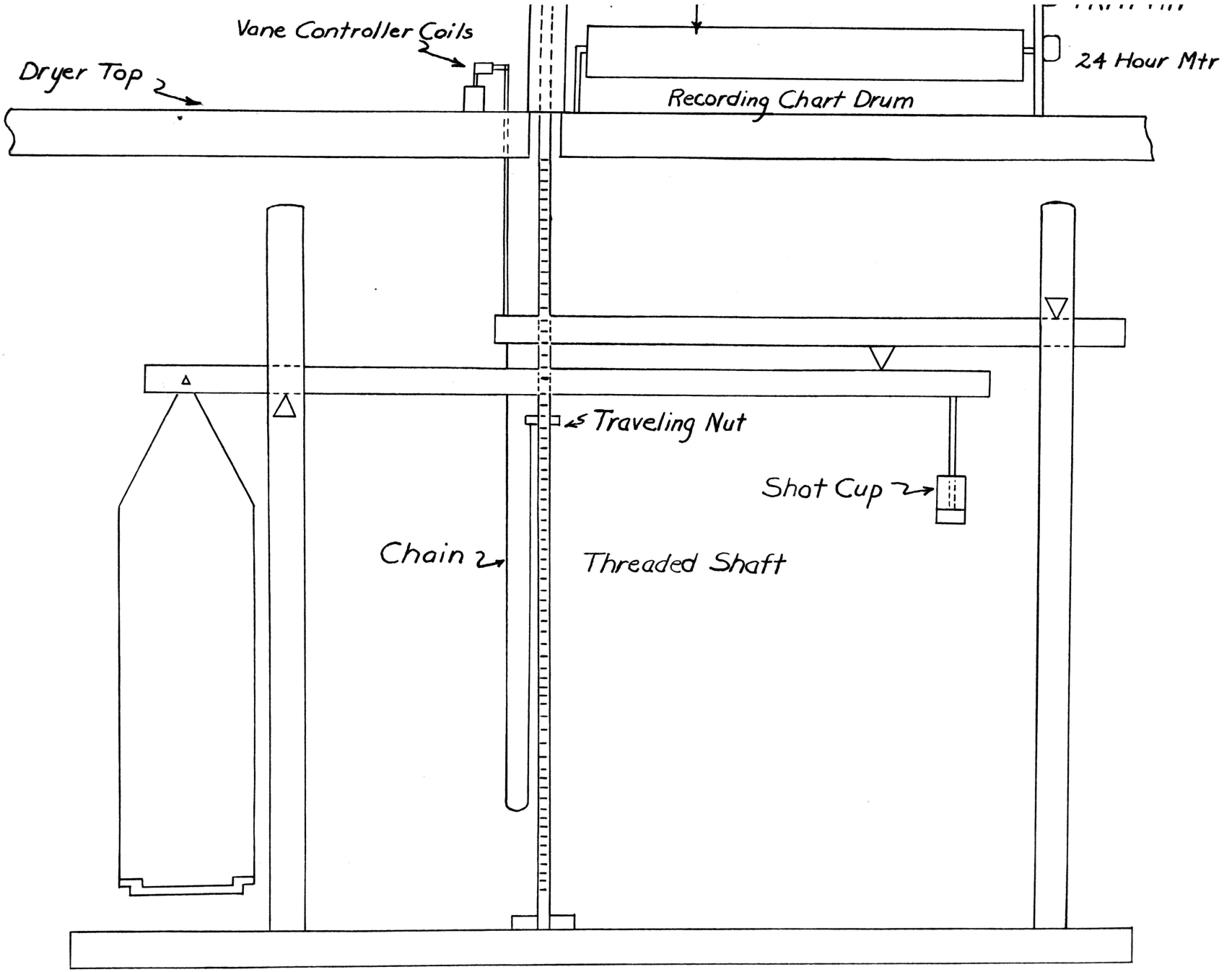
The motor drive is energized by a vane actuated controller which is patterned after a similar instrument manufactured by the Brown Instrument Co.[9] A circuit diagram is shown in Figure 3. The control unit is designed to make or break the electrical circuit with an extremely small movement of the vane. It operates on the principle that when a metal vane is gradually interposed between two oscillating coils, the state of oscillation can be made to change or stop, depending

(9) Brown Instrument Co. Electronics 19 (June 1947).



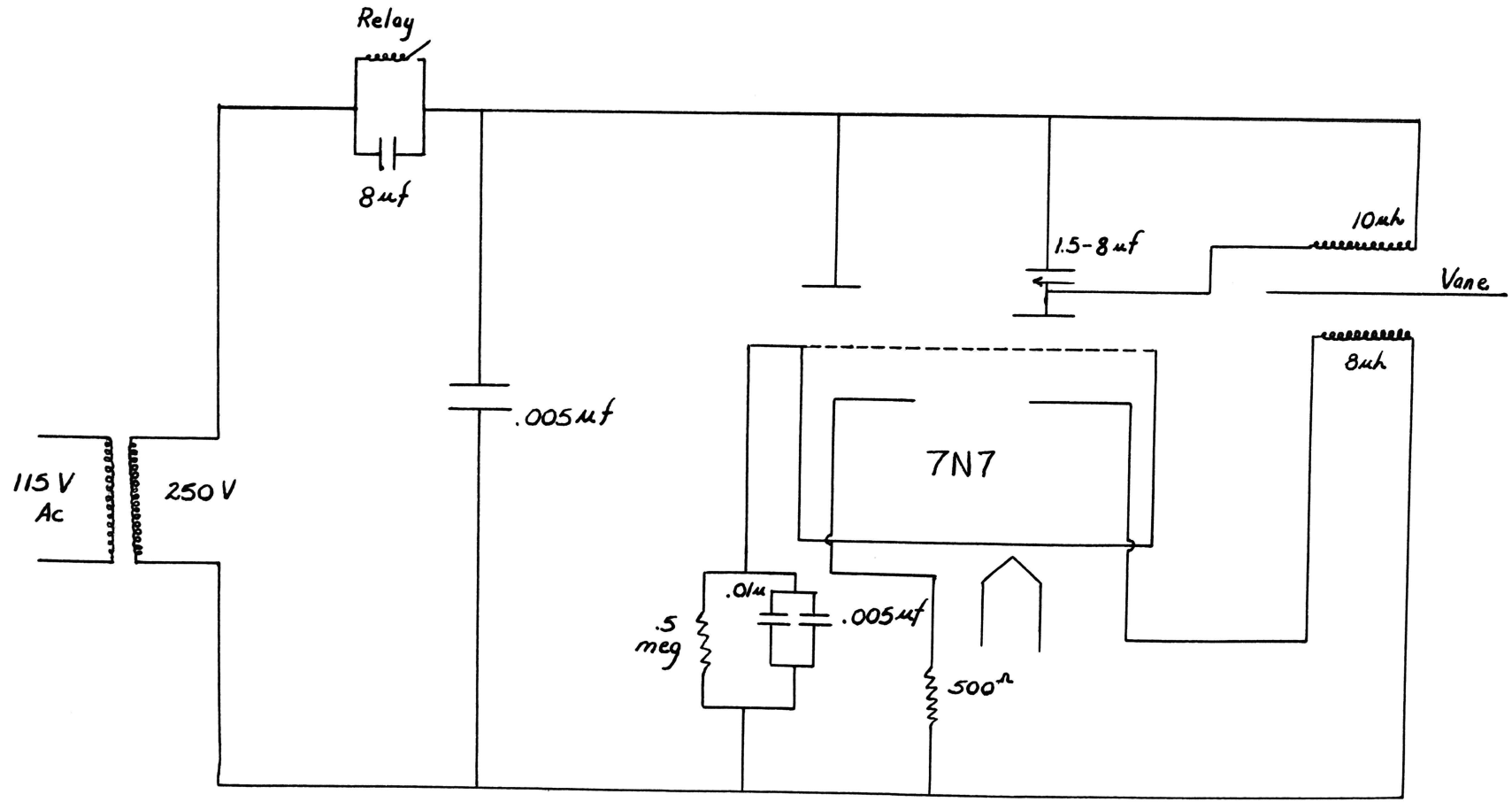
DRYER SCHEMATIC

ILLUSTRATION NO. 1



BALANCE MECHANISM SCHEMATIC

ILLUSTRATION NO. 2



VANE CONTROLLER CIRCUIT DIAGRAM

ILLUSTRATION NO. 3

upon the position of the vane. A sharp discontinuity exists between the presence and absence of oscillation. When oscillation is absent due to the vane position, the plate current from the 7N7 tube reaches a sufficiently high value to snap the relay to a closed position energizing the drive motor. A movement of the vane position 0.002 inches makes the difference between off and on with the controller. The oscillator coils are imbedded in plastic to minimize the effect of moisture escaping from the dryer cabinet.

Shrinkage is measured by a Gianninni Rectilinear Potentiometer of range 0–2000 ohms. The stem of the potemtiometer is connected by a fine wire to a weight placed atop the sample. A compression spring offers resistance to the downward movement of the potentiometer stem. As the sample shrinks the weight moving downward compresses the spring and brings with it the potentiometer stem. The change in potential drop between the variable and fixed terminals of the rectilinear potentiometer is measured with a Brown Recording Potentiometer, which may be calibrated in hundredths of an inch shrinkage. A Schematic diagram is shown in Figure 4.

SHRINKAGE APPARATUS

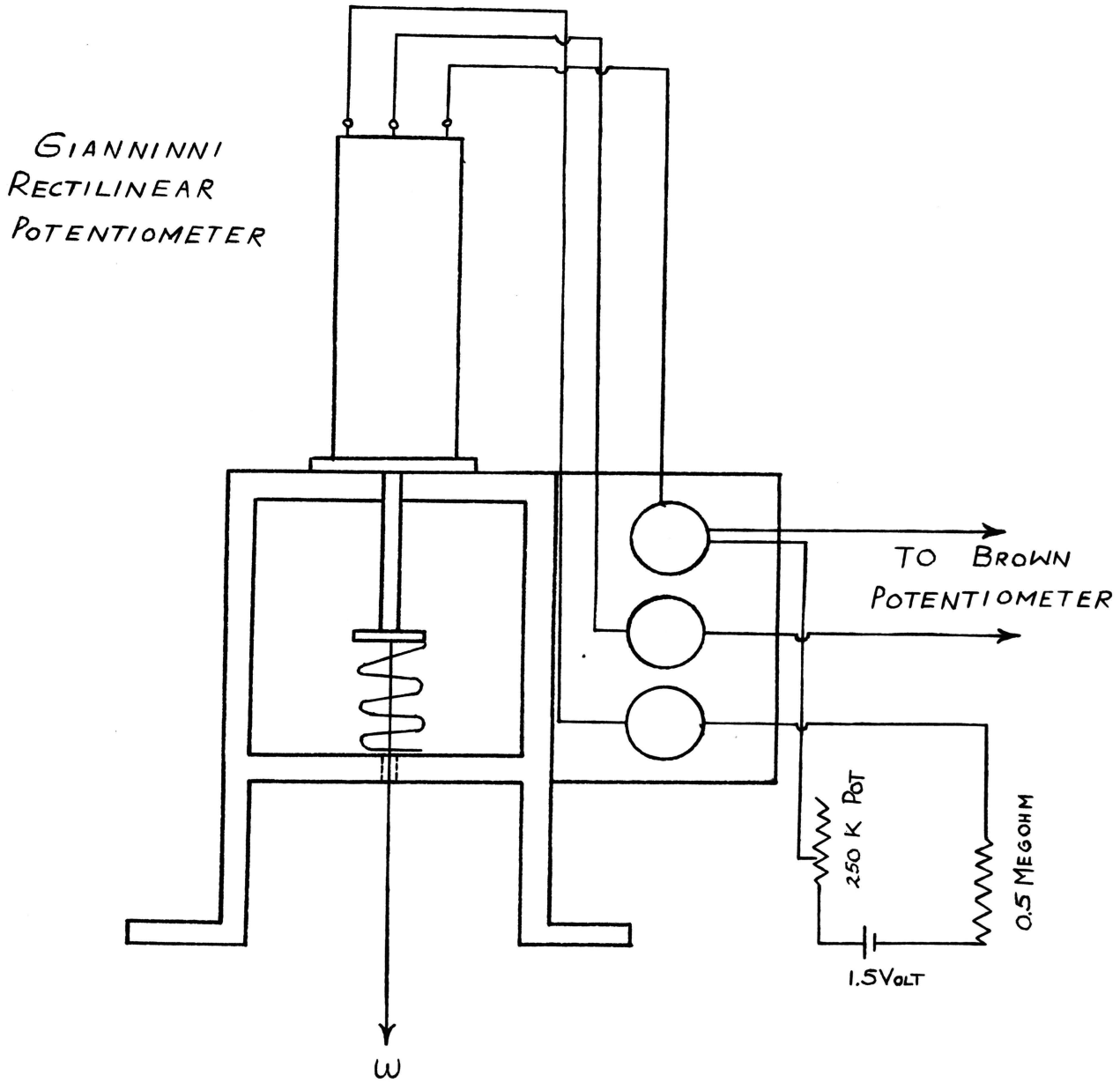


ILLUSTRATION 4

EXPERIMENTAL PROCEDURE

A spherical sample consisting of 1000 grams of No. 4 Kentucky Ball Clay and 1000 grams of Georgia Kaolin is prepared by dry mixing the two clays on a blunging rack and adding water to the extent of 800 gms. The plastic clay mass is then hand molded to a near spherical shape and the exact plastic weight determined. The sphere is then counter balanced on the chainomatic balance by placing lead shot in the cup extending from the opposite end of the folded beam. The weight attached to the rectilinear potentiometer is placed atop the sample, and the scale on the Brown Potentiometer adjusted to a position one fourth the full scale from the left end. This allows deflection in both directions, showing shrinkage or expansion.

The entire operation is then started. Initial Room conditions of wet and dry bulb temperatures are in the order of 60°F and 75°F respectively. The wet bulb temperature is increased to 140°F, the standard wet bulb temperature for all tests, at the rate of 10°F per hour, by controlled steam additions. This allows an eight hour preheating time which seems to be ample to uniformly heat the sphere all the way through, while at the same time it is sufficiently slow to prevent large amounts of condensation from appearing on the sphere surface.

During the entire preheating time the dry bulb temperature is maintained from 5° to 10°F higher than the wet bulb temperature by the steam addition.

After the eight hour preheating period, the dry bulb temperature is increased to 220°F where it is held constant for the remainder of the drying cycle.

The drying conditions of wet bulb temperature, dry bulb temperature and air velocity were maintained constant for the completion of the drying cycle, to allow any differences in the rate at which the drying was taking place to be characteristic of the drying mechanism.

After a period of approximately 20 hours after starting, the drum chart no longer indicates water loss, consequently the drying is complete down to the equilibrium water content point. This equilibrium water content is determined by the percent relative humidity, in that the sphere will not assume a lesser water content than the atmosphere surrounding it.

The dry weight is determined, along with the total water loss.

The drum chart record is them measured both horizontally and vertically for weight loss and time. Plotting these data on cross section paper weight loss as the ordinate and time as the abscissa then provides a curve upon which the slope is more readily measured. The slope of the above curve is then measured at small regular intervals and plotted vs. percent water content on the dry basis.

Variation of air velocity was obtained by surrounding the clay sphere with a hollow cylinder closed on the bottom. The air circulation then was effectively reduced to zero, with the removal of vapor being accomplished by convection to the air stream outside the cylinder. Air velocities in the order of 200 ft./min. were utilized

without the cylinder shield. To provide the 100-110 ft./min. air velocity small rectangular holes were cut in the bottom of the cylinder shield which would allow circulation of conditioned air past the sphere. The magnitude of the air velocities were determined by a paddlewheel type anemometer.

TABLE 1

Tabulation of Weight Loss - Time Data for designated curves

Figure 5

Time (Hours)	Weight Loss (Grams)
6.50	0
6.86	66.0
7.06	131.0
7.38	197.0
7.65	262.0
7.95	316.0
8.17	367.0
8.30	400.0
8.80	460.0
9.26	511.0
9.60	535.0
9.90	557.0
10.50	590.0
10.80	604.0
11.3	623.0
11.55	635.0
11.85	648.0
12.20	663.0
12.40	675.0
12.70	682.0
13.15	710.0
13.75	721.0
14.50	735.0
14.78	740.0
15.25	750.0
16.35	766.0
16.50	775.0
17.90	775.0

Figure 7

Time (Hours)	Weight Loss (Grams)
9.05	0
9.20	70.0
9.55	126.0
9.90	182.0
10.30	231.0
10.60	252.0
11.28	322.0
11.52	354.0
11.80	367.0
12.60	405.0
13.10	430.0
13.60	448.0
14.10	472.0
14.65	496.0
15.15	518.0
15.90	550.0
16.50	565.0
17.85	595.0
20.60	625.0

Table 2

Tabulation of Weight Loss - Time Data for designated curves

Figure 9		Figure 11	
Time (Hours)	Weight Loss (Grams)	Time (Hours)	Weight Loss (Grams)
9.60	50.0	7.32	0
10.00	90.0	7.55	35.2
10.60	150.0	8.05	98.5
11.32	224.0	8.30	166.0
11.68	259.0	8.80	254.0
12.10	315.0	9.40	366.0
12.44	342.0	9.80	446.0
12.80	388.0	10.20	469.0
13.10	425.0	10.62	507.0
13.48	450.0	10.90	543.0
14.10	484.0	11.15	578.0
14.20	505.0	11.48	592.0
14.85	550.0	11.71	616.0
15.40	575.0	12.0	626.0
15.90	600.0	12.70	655.0
16.55	624.0	13.40	680.0
17.65	670.0	13.68	690.0
18.40	690.0	14.10	715.0
20.80	749.0	14.75	725.0
21.60	770.0	15.30	746.0
		15.65	755.0
		16.50	765.0
		17.20	780.0
		20.00	780.0

DISCUSSION OF DATA

The curve of weight of water loss in grams vs. time in hours that appears in Figure 5 is characterized by a linear portion up to approximately 400 grams loss, and thence by a curved section decreasing in slope. Completion of the curve is 775 grams loss which represents the equilibrium water content for the dried sphere. At 500 grams loss this curve assumes for a short duration a near linear slope. The general shape of this preliminary curve is very much the same in all trials with changes in magnitude being brought about by external condition change.

Figure 6 represents the rate of water loss vs. percent water content on the dry basis. The analysis of this curve presents the key to the drying mechanism. It is seen that a straight line portion extends from the original water content down to a value of 19.8%. This means that the rate of evaporation which has a magnitude of 200 grams/hour is of constant value and exhibits the behavior of evaporation from a free liquid surface. This being the case the determining factors for the rate of evaporation are the same as for a free liquid surface, namely percent relative humidity, air velocity and dry bulb temperature. Under these conditions then the rate of internal water movement must be of sufficient magnitude even in this fairly large sphere so as to not be the limiting factor governing the drying rate.

Good agreement is then indicated with the work of Sherwood. Drying in this constant rate zone conforms to his Case I, in which

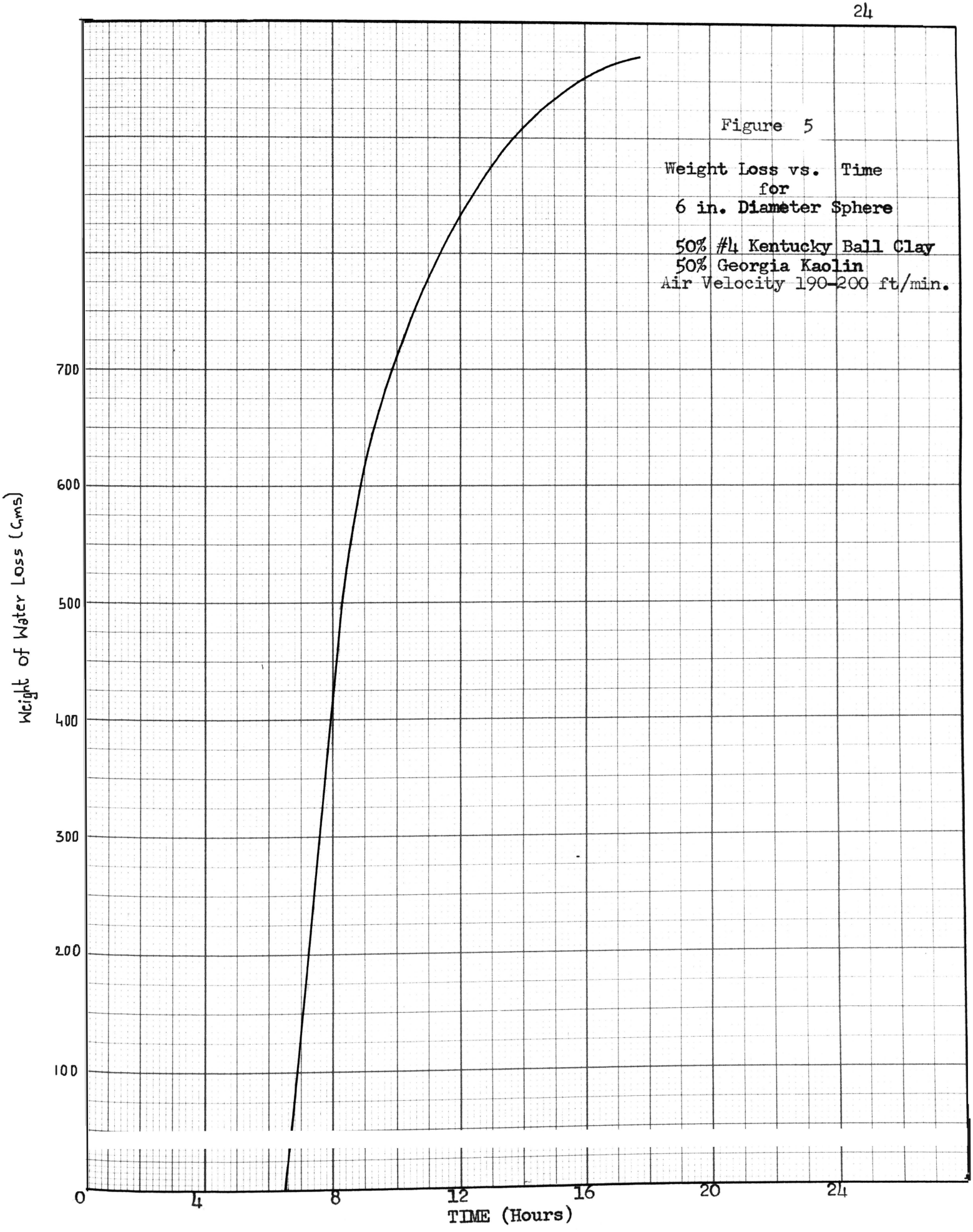


Figure 5

Weight Loss vs. Time
for
6 in. Diameter Sphere

50% #4 Kentucky Ball Clay
50% Georgia Kaolin
Air Velocity 190-200 ft/min.

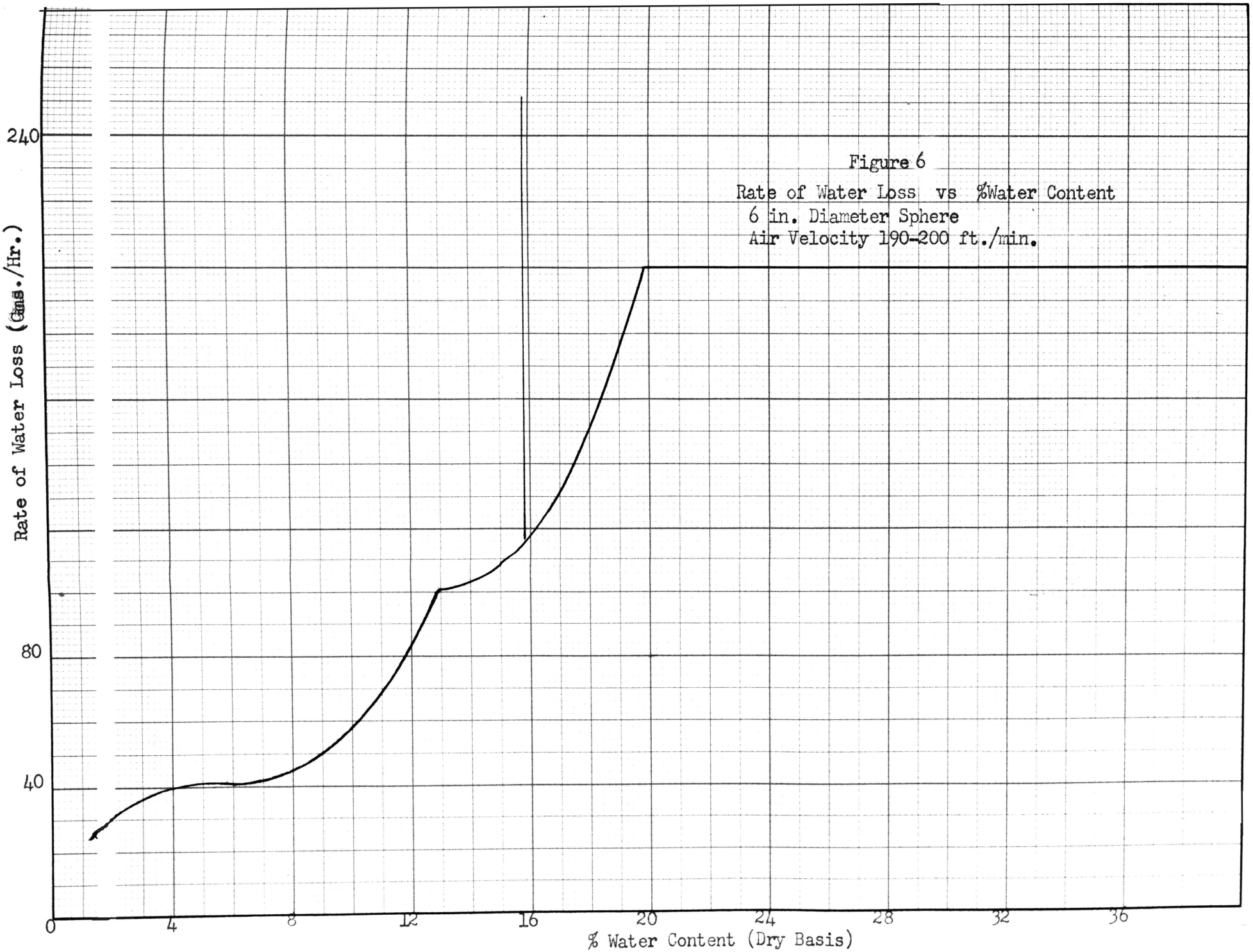


Figure 6
Rate of Water Loss vs %Water Content
6 in. Diameter Sphere
Air Velocity 190-200 ft./min.

resistance to liquid movement to the surface is small compared with the resistance to vapor removal from the surface.

The zone of constant rate becomes a falling rate period sharply at 19.80% water content. The falling rate period as named by Sherwood consists in itself of two separate zones. The zone of highest water content Sherwood terms the zone of decreased wetted surface, which for the application to clays is questionable, while the lower zone is one of liquid diffusion controlling. The division between these zones appears at 13% water content in the form of a small plateau. Shrinkage ceases at a water content of slightly less than 16%. When the sphere has completed shrinking, all the clay particles are understood to be in at least point contact with adjacent particles so that no further consolidation may take place. The bulk volume decreases from the time drying is initiated until shrinkage ceases and from then on remains constant, while water loss occurs from the remaining water films about each clay particle and from the pores and voids. At a water content of slightly above 13% or at the plateau of the curve the surface of the sphere was observed to become lighter in color indicating that the surface itself was drying and the plane of vaporization was receding inward.

The second portion of the falling rate period which Sherwood designates the zone of liquid diffusion controlling is concave upward through 6% and them becomes concave downward. Norton[10] indicates that a residual kaolin undergoes an expansion in this range

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(10) Norton, F. H.
ob. cit. p. 106-114.

of water content, and so being the case it is readily seen that the resistance to both vapor and liquid diffusion if this is the mechanism would be less with a more permeable structure.

The significance of the plateau is not readily apparent. In all probability immediately at the end of the plateau there is a recession of the plane of vaporization, but what causes the near constancy of the rate of water loss will be discussed subsequently. Note should be taken of the 190-200 ft./min. air velocity, which directly determines the 200 grams/hour maximum rate of water loss.

Figure 8 is the rate curve for the decreased air velocity (100-110 ft./min.) obtained by partially shielding the sphere with a hollow cylinder. The rate of water loss during the constant rate zone has been decreased from 200 grams/hour down to 135 grams/hour with a shift to the left in the termination of the constant rate zone from 19.8% to 17.00% water content. This is another sound reason to believe that the limiting factor for rate of water loss is the resistance offered to vaporization from the surface. Although a similar sphere is used, the same wet and dry bulb temperatures employed, an entirely different rate is obtained and between the water contents of 17% and 19.8% the drying mechanism is apparently different for the two spheres. The same general shape appears in Figure 8 as in Figure 5, with the lower water contents indicating a lower resistance to diffusion of either vapor or liquid due probably to kaolin expansion.

Figure 10 shows the rate curve for a completely shielded sphere, which results in an air velocity of effectively zero.

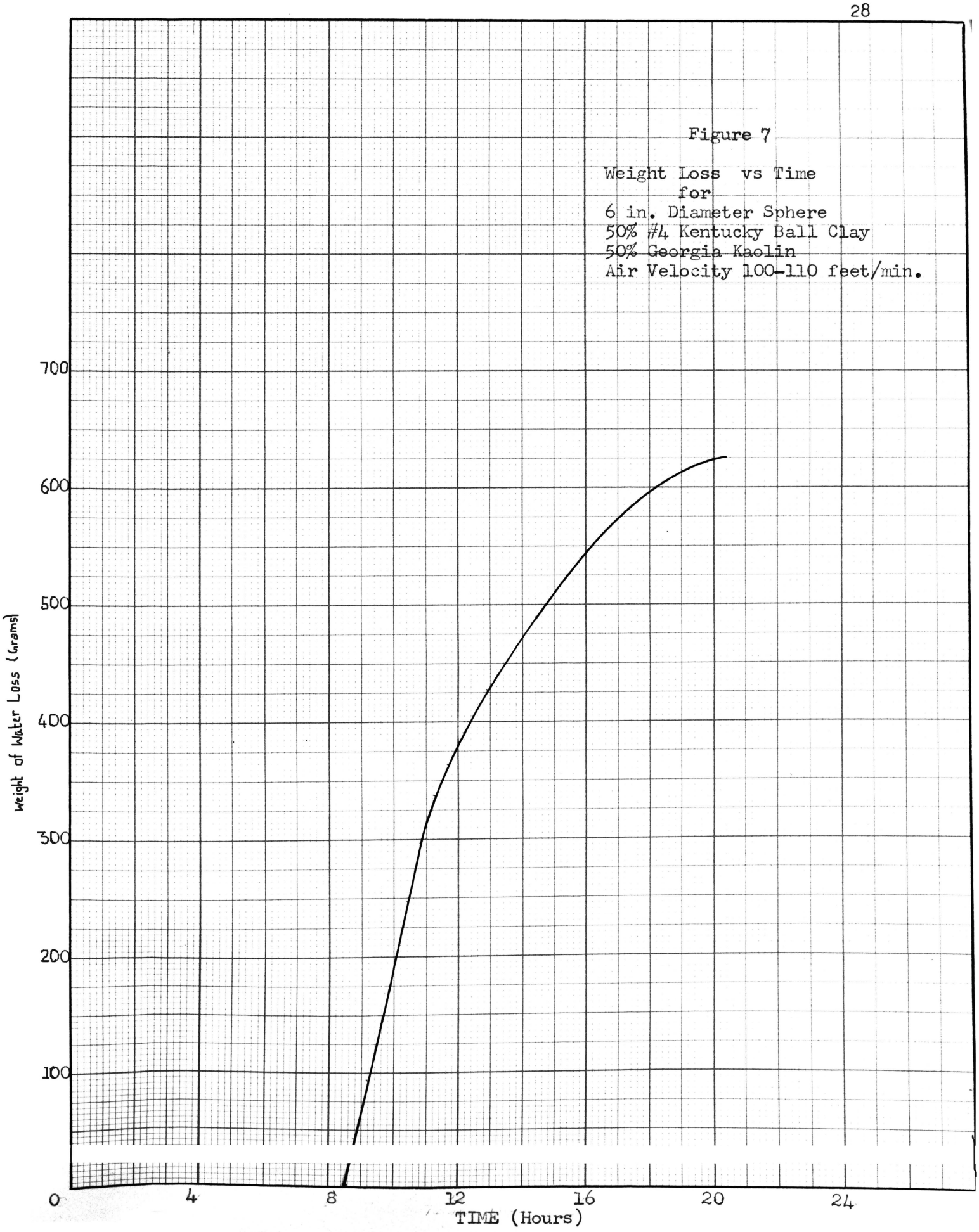
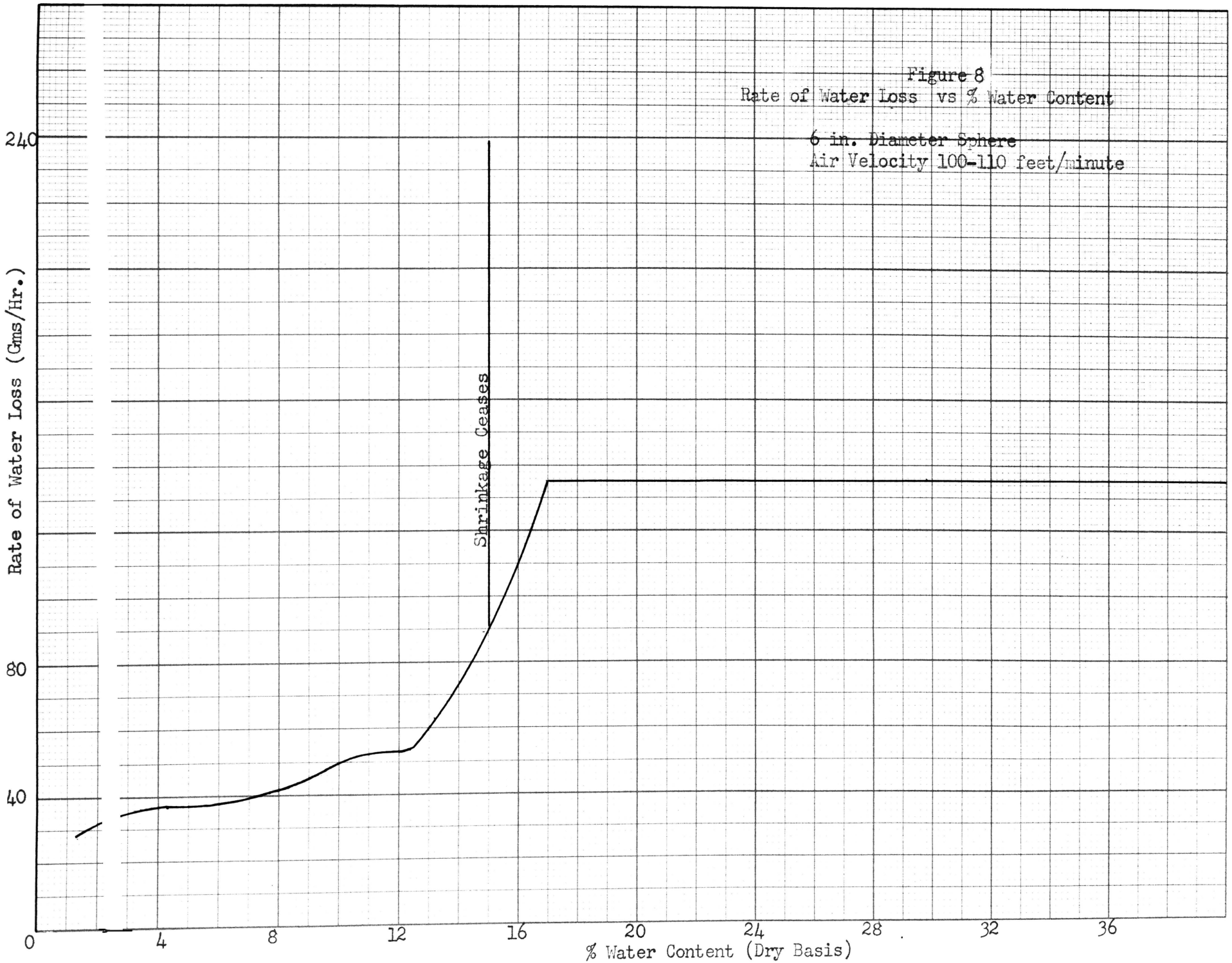


Figure 7
Weight Loss vs Time
for
6 in. Diameter Sphere
50% #4 Kentucky Ball Clay
50% Georgia Kaolin
Air Velocity 100-110 feet/min.
Weight of Water Loss (Grams)
700
600
500
400
300
200
100
0
4
8
12
16
20
24
TIME (Hours)

Figure 8
Rate of Water Loss vs % Water Content

6 in. Diameter Sphere
Air Velocity 100-110 feet/minute



The vapor removal is accomplished by natural convection out of the hollow cylinder. Any heating of the sphere by radiation from the Chromalox units is also eliminated. The zone of constant rate continued in this trial to 14.8% water content at a water loss of 100 grams/hour, and the shrinkage ceased at 14.95% before the termination of the constant rate period. The remaining portion of the curve resembles the others discussed.

The above 3 curves present some very interesting conjectures. Starting with the widely accepted contention presented by Norton(11) that a clay when wetted develops a water film around each particle and that the particles and water films as a single unit are separated from other units by free water which acts as a lubricant, a mechanism analysis should be forthcoming.

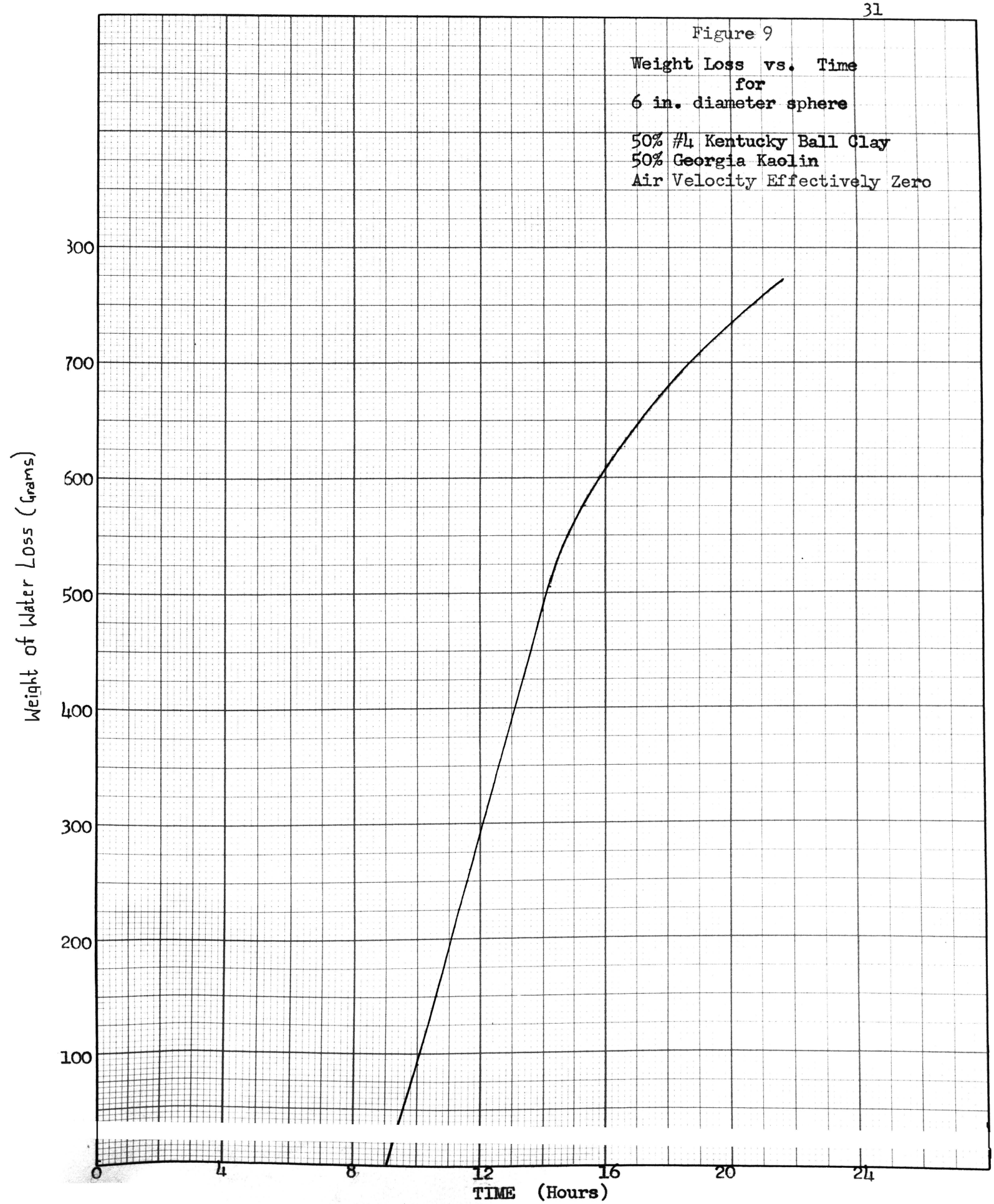
Considering Figure 5 with initial water content of in the order of 40% of the dry weight, the rate of water loss is constant at 200 grams/hour down to 19.8%. In this zone we have either one of two extreme cases or an intermediate thereof in existence. The resistance to water movement to the surface could remain a constant which is quite unlikely or the resistance to water movement starts at some relatively low value at the initiation of drying and continually increases until at the break point this resistance to liquid flow exceeds the resistance to vapor removal when 200 grams of water per hour are evaporating from the surface. At intermediate water contents this resistance to liquid movement would be at all times less than the resistance to vapor removal. Retaining in mind the fact that

(11) Norton, F. H. - Ibid.

Figure 9

Weight Loss vs. Time
for
6 in. diameter sphere

50% #4 Kentucky Ball Clay
50% Georgia Kaolin
Air Velocity Effectively Zero



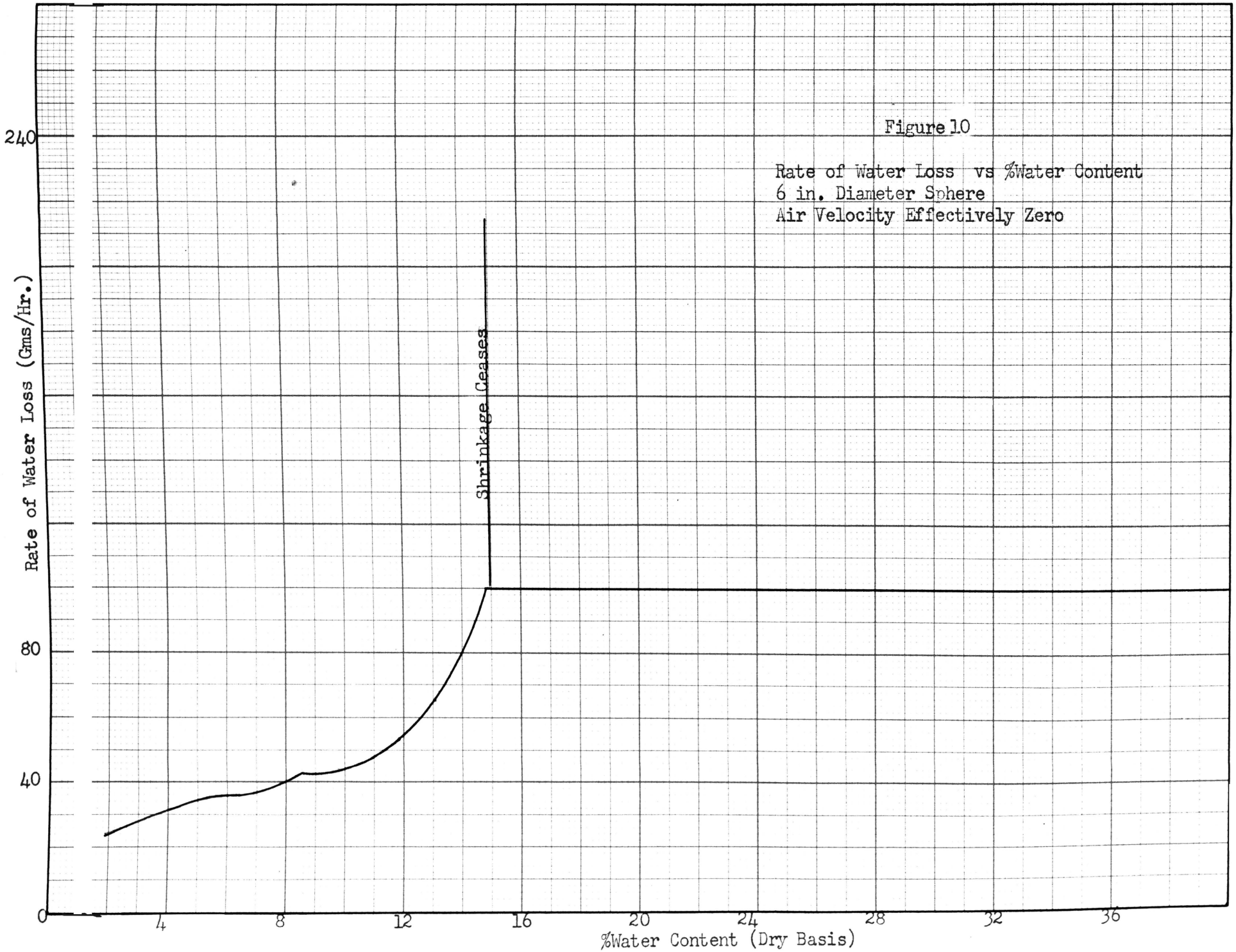


Figure 10

Rate of Water Loss vs %Water Content
6 in. Diameter Sphere
Air Velocity Effectively Zero

clay particles have a rather strong affinity for water and that this affinity decreases outward from the clay particle through the water film, some point in the thickness of the water film must exist where the resistance to its removal plus the inherent movement difficulties balances the resistance to vapor removal from the surface. Using this supposition this balance point may only occur at the break point in the curve. As more water is removed from the water films and their thickness is decreased the resistance to movement would increase. This follows the reasoning above in that the attractive forces that clay maintains for water which are difficult to define quantatively increase as the film edge moves closer to the clay particle. This behavior is evidenced by the rapidly decreasing slope in this zone, which Sherwood named the zone of decreased wetted surface.

The removal of water from the films continues until the shrinkage ceases and the clay particles are in point contact. The remaining water exists in the void or pore spaces, and in a hydrated layer surrounding the particles.

The mechanism of water movement to the surface is either capillarity of diffusion, or both throughout the whole process. The empirical relationship for diffusion as presented by Norton(12) depends for its existence on a concentration gradient being established. Troop and Wheeler(13) present curves showing that this gradient on cylinders drying from the end surface only is in the

(12) Norton, F. H. - Ibid.

(13) Troop, R. S. and Wheeler, F.
Trans. Brit. Cer. Soc. 26, 244 (1927).

order of 5% difference at 5 inches from the surface. An indication is then presented that diffusion plays little part in the constant rate zone, because water may move to the surface with fair rapidity preventing the formation of a concentration gradient. Another very good argument for small concentration gradients during the shrinkage period is the rapidity with which this large sphere is drying, without failure. With water removal in the zone of constant rate of 200 grams/-hour and the total drying time 24 hours or less, a very large gradient would surely lead to cracking.

By the elimination process it is then concluded that mainly capillarity drains water from the interior of the ware to the surface during shrinkage which is in general agreement.

When shrinkage ceases, however, the bulk volume no longer decreases as further water is lost. As a consequence air must diffuse inward through the surface to take the place of water removed. This further increases the difficulty of water movement to the surface, which then would promote the existence of concentration gradients and in turn diffusion. The only plausible explanation for the plateau, or short nearly constant rate period occurring immediately before the second break in the curve, is the simultaneous existence of both diffusion and capallarity. Apparently diffusion is becoming more pronounced and capallarity of lesser importance, with the combined effect preventing a rapid decline in the rate valve. The surface was observed to become dry in the plateau range of water contents which means a recession inward of the vaporization plane. The further difficulties presented by vapor diffusion out of the sphere, and air diffusion into the sphere account for the decreasing

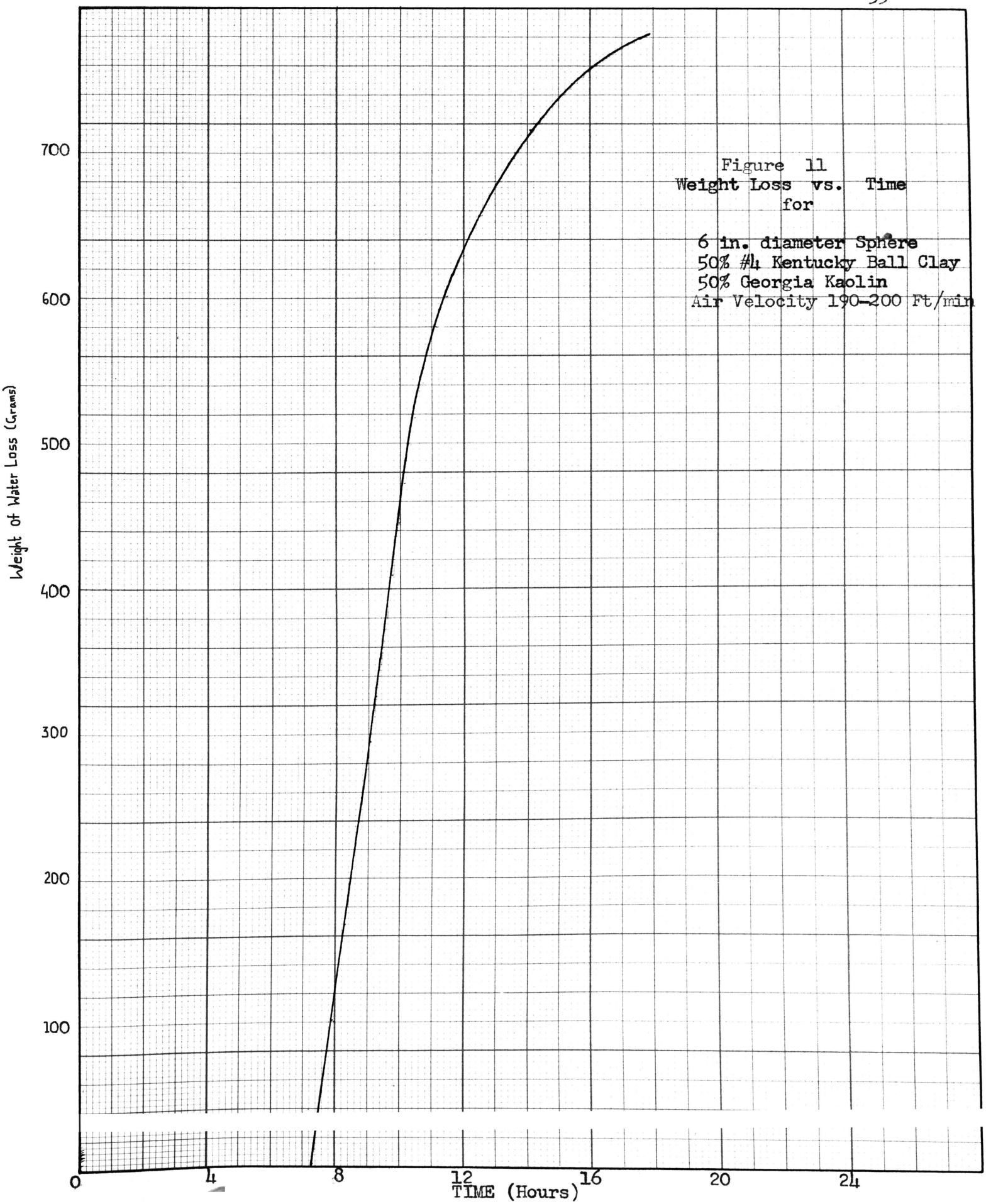


Figure 11
Weight Loss vs. Time
for

6 in. diameter Sphere
50% #4 Kentucky Ball Clay
50% Georgia Kaolin
Air Velocity 190-200 Ft/min

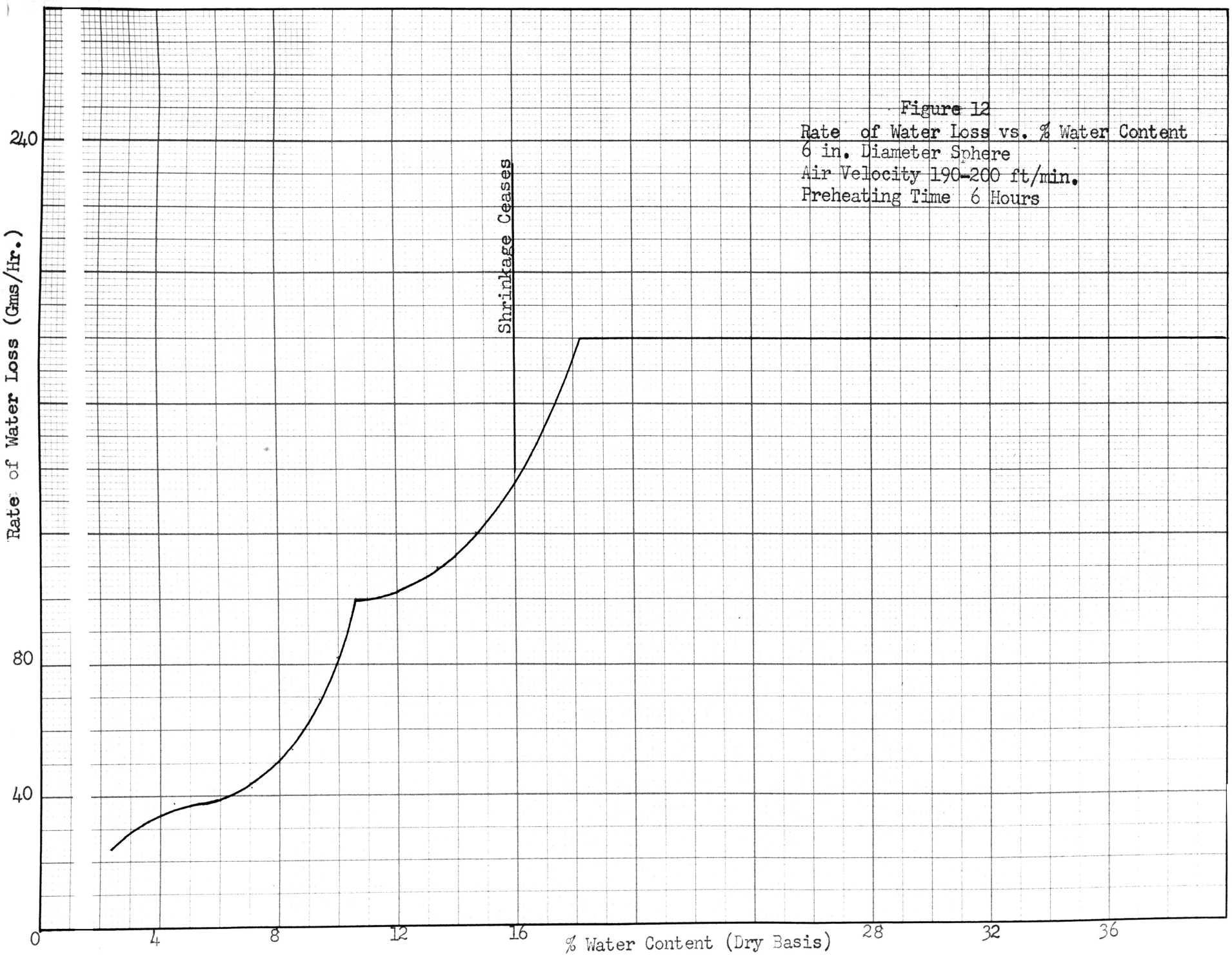


Figure 12
Rate of Water Loss vs. % Water Content
6 in. Diameter Sphere
Air Velocity 190-200 ft/min.
Preheating Time 6 Hours

slope after the plateau. Considering Figure 10 once again an explanation must be presented to account for the increased length of the constant rate zone. By virtue of the constant rate in this zone the controlling mechanism is the resistance to vapor removal from the surface, which of course is less for a 100 gram/hour loss than for a 200 gram/hour loss.

Superimposing the additional axis of permissible rate of flow to the surface, on the rate of water loss - % water content curve, provides an interesting picture. The permissible rate of flow is plotted as a right hand ordinate and the magnitude of this rate is determined by the resistance offered by the sphere to water movement to the surface.

The normal rate of loss-percent water content curve then is a division line between safe drying conditions and unsafe drying conditions at the prescribed ware temperature of 140°F. The area to the right of the curve is a safe drying area while that to the left will result in the sample cracking, due to case hardening or the premature recession of the plane of vaporization into the ware. The length of the constant rate zone is then a laboratory measure of the ease with which clay under the predetermined conditions will dry under industrial conditions.

Figure 12 in an oblique manner points to the value of preheating the sample. The preheating time was reduced from 8 hours to 6 hours for this trial. As a consequence the rate of water loss was not the usual 200 grams/hour but 180 grams/hour. In all probability a temperature gradient was set up in the sphere and as a result the overall temperature

was less at the outset of drying which made the process of vaporization at the surface more difficult.

The results of a final trial are not shown herein although the ramifications therefrom are worthy of inclusion. An attempt was made to dry a sphere without any preheating, simply placing it in the atmosphere of 140°F wet bulb and 220°F dry bulb. Condensation of course appeared on the surface but not to such an extent as to cause slumping. The sphere in drying only through what would be normally the constant rate period developed enough cracks to be a complete failure, indicating that these spheres could not be dried at this accelerated schedule without bringing the temperature of the sphere up to near 140°F.

It has been suggested by Dr. T. J. Planje[14] that the zone of decreased wetted surface as named by Sherwood would be better named the zone of decreasing pores. This has merit in that Sherwood's original work was in the drying of paper pulp, wood fibers, leather and other such materials and undoubtedly a decrease in the wetted surface is experienced because of the drying of the many surface projections. For the applications to clays however it does not seem feasible that much drying surface is decreased until the vaporization plane moves away from the surface. On the other hand it is during the final stages of shrinking, which constitutes most of this zone, that the pores or capillaries are actually being closed because of contact between clay particles. For these reasons then the name of zone of decreasing pores is quite applicable.

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(14) Planje, T. J.
Prof. of Cer. Eng. Univ. of Mo. School of Mines & Met.

CONCLUSIONS AND SUMMARY

The zone of constant rate appears to be without question, variable on a percent of water content basis, depending upon the rate of water loss which external conditions of wet bulb temperature, dry bulb temperature and air velocity establish. The rate of water loss in the constant rate zone under any external conditions is limited by the resistance to water vaporization from the surface. Termination of shrinkage does not lead to an abrupt change in the rate curve as one would expect, but it does lead to a near constant rate plateau, and occurs at a water content located in the zone of decreasing pores.

The zone of decreased wetted surface as presented by Sherwood is more suitably named the zone of decreasing pores, because it is during this period that pores and capillarities are being closed due to the clay particle consolidation.

Using ware of large cross section allows the resistance to internal liquid movement to define the nature of the drying process, thus the utilization of spheres with minimum surface to volume ratio provides the extreme case.

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VITA

Robert F. Grady III was born June 19, 1929 in St. Louis, Missouri to Mr. and Mrs. Robert F. Grady Jr.

He attended Roe Grade School in St. Louis until the 7th grade when his parents moved to Ladue, a suburb of St. Louis where he finished grade school. The 9th grade was spent at Hanley Junior High School and the 10th at Clayton High School.

At this point his father accepted the position of Production Manager for the Mason City Iowa Brick and Tile Company. It was in Mason City that he graduated from high school in May of 1946.

June 24, 1946 he enlisted in the Army and upon completion of basic training was sent to Korea with the 6th Infantry Division. On November 13, 1947 he was honorably discharged with the rank of Sergeant.

The spring semester of 1948 he enrolled in Mason City Junior College and transferred the following semester to Simpson College at Indianola, Iowa. In September of 1949 he enrolled at the University of Missouri School of Mines and Metallurgy in the Ceramic Engineering Curriculum where he graduated in May of 1952.

While at M.S.M. he joined the following societies and fraternities. Lambda Chi Alpha, Theta Tau, Sigma Gamma Epsilon, Keramos and the American Ceramic Society student branch.

During the fall of 1952, and both semesters of 1953 he held an Assistantship in the Department of Metallurgy while working towards the degree of Master of Science in Ceramic Engineering.